

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

(12) UK Patent Application (19) GB (11) 2 303 857 (13) A

(43) Date of A Publication 05.03.1997

(21) Application No 9615231.9	(51) INT CL ⁶ C08L 83/04
(22) Date of Filing 19.07.1996	
(30) Priority Data (31) 08508407 (32) 28.07.1995 (33) US	(52) UK CL (Edition O) C3T THC T201 T210 T521 T545 T549 T572 T621 U1S S1343 S1377 S1399
(71) Applicant(s) General Electric Company (Incorporated in USA - New York) One River Road, Schenectady, NY 12345, United States of America	(56) Documents Cited EP 0463431 A Abstracts of JP 07173294 A (Shinetsu Chemical Ind. Ltd.) Abstracts of JP 07041416 A (Shiseido Co. Ltd.) Abstracts of JP 05311575 A (Sanyo Chem. Ind. Ltd.)
(72) Inventor(s) Makoto Matsumoto James Hale Merrifield Frank John Traver	(58) Field of Search UK CL (Edition O) C3T THC THF INT CL ⁶ C08G 77/06 77/08 77/10 , C08L 83/00 Online: CAS-ONLINE, EDOC, JAPIO, WPI
(74) Agent and/or Address for Service Anne C Szary GE London Patent Operation, Essex House, 12-13 Essex Street, LONDON, WC2R 3AA, United Kingdom	

(54) Stabilised anionic emulsion-polymerised silicone emulsions

(57) Anionically emulsion polymerized silicone emulsions may be converted to cationic emulsions by first treating with a nonionic surfactant having an HLB ratio greater than 9 followed by treating with cationic quaternary ammonium surfactants.

The stable oil-in-water emulsion are prepared by:

- (a) blending a mixture of silicones with water and an anionic surfactant which is preferably an alkyl, aryl or aralkyl sulphonic acid;
- (b) heating at 75 to 98°C for 1 to 5 hours;
- (c) cooling;
- (d) adding a compatibilising nonionic surfactant with HLB ≥ 9;
- (e) adding a cationic surfactant.

The compositions are useful in personal care products, particularly for the hair.

GB 2 303 857 A

CATIONIC SURFACTANT COMPATIBLE ANIONIC EMULSION
POLYMERIZED SILICONE EMULSIONS

The present invention relates to selection of precursors and methods of preparation of emulsion polymerized silicones wherein said silicones are polymerized in the presence of an anionic surfactant resulting in a silicone emulsion and wherein said resulting silicone emulsions are compatible with cationic surfactants. Such silicone emulsions are useful in a variety of personal care products.

Background of the Invention

Emulsion polymerization of silicone polymers to prepare high molecular weight emulsified silicone polymers are well-known in the art. An early example of such technology has been disclosed in U. S. patent 2,891,920 and teaches the polymerization of octamethyltetrasiloxane (D₄) and other silicone oligomers using a strong base in the presence of quaternary ammonium compounds. This technology has been extended as taught in U. S. patent 3,294,725 to include the use of sulfonic acids to effect the polymerization of silicone oligomers. Polymerization of silicone oligomers in the presence of sulfonic acids is particularly effective in producing high molecular weight silicone polymers.

It is a well recognized feature of the polymerization kinetics of silicone oligomers that low molecular weight polymers result from the initial ring opening polymerization. It has been found that control of the cooling step occurring after heating the reaction mixture containing the silicone oligomers to achieve the initial polymerization results in control of the degree of polymerization of the silicone. The extent of polymerization is kinetically controlled by approach to equilibrium and the temperature at which equilibrium is established. Generally, anionic polymerization catalysts allow for a rapid approach to equilibrium at all temperatures, in contrast to cationic polymerization catalysts where the approach to equilibrium is significantly slower. This results in a reliance on anionic polymerization catalysts in the

BAD ORIGINAL

commercial manufacture of silicone polymers, if high molecular weight polymers are desired.

The convenience afforded by the rapid reaction rates achievable with anionic polymerization catalysts, particularly in emulsion polymerization, 5 limits the applications to which the resulting polymerized silicone emulsions may be used. While they may generally be employed in a variety of applications, including cosmetic applications, a change in the ionic balance of the emulsion frequently results in a break-up of the emulsion. Thus, treatment of an emulsion polymerized silicone emulsion, polymerized in the 10 presence of an anionic polymerization catalyst, with a cationic surfactant for example will generally destroy the emulsion. As hair care products are typically required to possess cationic properties due to the weakly anionic nature of human hair, this leads to significant formulation difficulties in 15 using emulsion polymerized high molecular weight silicone emulsions in human hair cosmetic and personal care products. In hair care applications, it is advantageous to use silicone emulsions containing cationic polymers for improved deposition on hair surfaces. It is also desirable to deposit high 20 molecular weight silicone polymers on the hair because of the enhanced conditioning properties possessed by high molecular weight silicone polymers in contrast to low molecular weight silicone polymers.

The typical solution to this problem is to produce emulsion polymerized silicone emulsions that are polymerized in the presence of a cationic polymerization catalyst. However, emulsions produced in this fashion require long holding times to achieve the desired molecular weight of 25 silicone polymer. Thus, ideally it would be desirable to be able to prepare high molecular weight silicone polymers by emulsion polymerization using anionic surfactants and then modify the product in some fashion to achieve the desired cationic properties that impart beneficial results to hair care formulations.

30 The simple expedient of adding cationic surfactants to high molecular weight silicone polymer emulsions that have been prepared using anionic surfactants is known to be a method of breaking up the emulsion. Adding a surfactant of opposite conjugate properties is a generally recognized technique for breaking emulsions. This is exemplified by a process for 35 coagulating a grafted rubber compound as disclosed in U. S. 4,831,116 where the emulsion is prepared by a polymerization process in the presence of an

BAD ORIGINAL

anionic surfactant and the emulsion is broken and coagulated by the addition of a cationic surfactant.

There are some recent advances that indicate in certain isolated systems it is possible to preserve the emulsion when both cationic and anionic surfactants are present. As disclosed in U. S. 4,401,788, a vinylidene latex system produced by emulsion polymerization in the presence of an anionic surfactant tolerated the addition of a cationic surfactant. This particular system however, had a limited stability of the resulting emulsion. As disclosed in U. S. patent 5,045,576, anionic asphaltic emulsions can be converted to cationic emulsions through the addition of cationic surfactants in conjunction with a so-called steric stabilizer that prevents break-up or breakage of the emulsion. Neither of these systems deals with silicone polymer emulsions, nor would it be reasonable to expect that the techniques usable in latexes or asphalts would be directly transferable to silicone emulsions.

Summary of the Invention

We now disclose that these prior art problems have been solved, enabling the preparation of cationic surfactant compatible high molecular weight silicone polymer emulsions that are initially prepared using anionic surfactants. These emulsions can be achieved by limiting the selection of reactants to narrow classes of reagents and this selection enables the use of certain cationic surfactants after the emulsion has been prepared.

The present invention thus provides for a stable cationic silicone oil-in-water emulsion comprising:

- (a) a silicone polymer having a viscosity ranging from about 10,000 to 10,000,000 centistokes;
- (b) an anionic surfactant selected from the group consisting of alkyl, aryl and alkaryl sulfonic acids where the alkyl group ranges from 1 to about 20 carbon atoms, the aryl groups range from 6 to 30 carbon atoms, and the alkaryl groups range from 7 to about 50 carbon atoms;
- (c) a compatibilizing surfactant having a hydrophilic lipophilic balance ratio of about 9 or greater; and
- (d) a cationic surfactant selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides, mono-methyl ethoxylated ammonium sulfate, alkyl trimethyl ammonium halides, and

BAD ORIGINAL!

alkyl trimethyl sulfate where the alkyl group of said cationic surfactant ranges from about 9 to about 30 carbon atoms.

The present invention further provides for a process for making a stable cationic silicone oil-in-water emulsion comprising:

- 5 1) blending a mixture of silicones selected from the group consisting of cyclic silicone oligomers, mixed silicone hydrolyzates, silanol stopped oligomers, higher molecular weight silicone polymers, and functionalized silicones with
- 10 2) water, and
- 10 3) an anionic surfactant;
- 10 4) heating the blend to a temperature ranging from about 75 to about 98 °C for a period of time ranging from about 1 hours to about 5 hours;
- 10 5) cooling the heated blend to a temperature ranging from 0 to about 25 °C for a period of time ranging from about 3 hours to about 24 hours;
- 15 6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactants having a hydrophilic lipophilic balance (HLB) ratio greater than 9; and
- 15 7) adding a cationic surfactant.

The compositions and processes of the present invention are useful for personal care compositions and the preparation of personal care products. Such products include but are not limited to personal cleansing products, lotions, shampoos, hair coloring compositions, conditioners, rinses, neutralizing lotions, creams, gels, mousses, aerosols, and pump sprays and the like.

Detailed Description of the Invention

- 25 The present invention is based on the discovery that certain cationic and anionic surfactants are compatible with one another in the presence of certain other stabilizing surfactants and that emulsions prepared via an anionically catalyzed emulsion polymerized may be converted by means of these special classes of surfactants to cationic emulsions without breakup or destruction of the emulsion. A significant advantage of this discovery is that silicones may be rapidly polymerized via an anionic emulsion polymerization, which as a reaction class, has significantly faster polymerization kinetics than cationic emulsion polymerization and subsequently converted to a cationic emulsion. The consequential advantage 30 of this discovery is that many cosmetic products preferentially utilize cationic
- 35

BAD ORIGINAL

emulsions because certain components, particularly silicones, are deposited on the hair or skin more easily when the emulsion is cationic.

By polymerization Applicants are specifically referring to the polymerization of cyclic silicones or other silicone oligomers under conditions of anionic emulsion polymerization. Emulsion polymerization of silicone oligomers or cyclic silicones takes place rapidly at temperature ranging from about 75 to about 98 °C. Once the initial polymerization at this temperature is accomplished, generating polymers of intermediate chain length which silanol terminations, cooling to about 0 to 25 °C allows a further silanol condensation to occur with a subsequent increase in molecular weight. Generally, this low temperature silanol condensation occurs much more rapidly under anionic conditions as contrasted with cationic conditions. This has heretofore presented a dilemma to the cosmetic industry because the favored emulsions are cationic and they are generally prepared by polymerization techniques that have slow reaction kinetics. While anionic polymerization techniques such as anionic emulsion polymerization enjoy rapid kinetics previous attempts to convert the resulting anionic emulsions to cationic emulsions have generally resulted in a breakup of the emulsion. Anionic emulsion polymerization results in a polymer which when isolated as a distinct, pure, homogeneous phase has a viscosity ranging from 10,000 to 10,000,000 centistokes. Applicants define high molecular weight silicone polymers to mean polymers which have a viscosity ranging from 10,000 to 10,000,000 centistokes.

Since Applicants' discovery involves stability of the resulting emulsion, Applicants define stability to mean the absence of a lack of separation, creaming, creaming or sedimentation. Stability has been determined using procedures analogous to those defined in ASTM test method D3716 (15:04), 1991. Further, stable emulsions are defined as those emulsions which remain unaffected by storage at a temperature ranging from about 50 to about 60 °C for a period of time of at least three days.

In one embodiment of the process of the present invention, the desired emulsion is prepared by preparing an emulsion polymerized silicone utilizing the following procedure:

1) blending a mixture selected from the group consisting of cyclic silicone oligomers (e.g. trimer, tetramer, pentamer and hexamer), mixed

BAD ORIGINAL

silicone hydrolyzates, silanol stopped oligomers, higher molecular weight silicone polymers, and functionalized silicones with

2) water, and

3) anionic surfactants selected from the group consisting of alkyl, aryl,

5 and alkylaryl sulfonic acids, where the alkyl groups are 1 to 20 carbon atom alkyl groups and the aryl groups are 6 to 30 atom aryl groups;

4) heating the blend obtained by mixing the silicone, water and surfactant to a temperature ranging from about 75 to about 98 °C for a period of time ranging from about 1 hours to about 5 hours;

10 5) cooling the intermediately emulsion polymerized silicone to temperature ranging from 0 to about 25 °C for a period of time ranging from about 3 hours to about 24 hours;

6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactants having a hydrophilic lipophilic balance (HLB)

15 ratio greater than 9; and

7) adding a cationic surfactant selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides or sulfates and alkyl trimethyl ammonium halides or sulfates, where the alkyl group ranges from eight to thirty carbon atoms.

20 In the anionic emulsion polymerization step, the acid catalyst is selected from the group consisting of alkyl sulfonic acids, aryl sulfonic acids, or alkyl aryl sulfonic acids where the alkyl group ranges from one to twenty carbon atoms and the aryl group ranges from six to thirty atoms. Preferably the catalysts are selected from the group consisting of benzene sulfonic acid, xylene sulfonic acid, dodecylbenzene sulfonic acid, and twelve to eighteen carbon atom alkyl group alkyl sulfonic acids.

When completed, the anionically emulsion polymerized silicone emulsion resulting is treated with a nonionic surfactant having an HLB ratio greater than 9, preferably greater than 10, more preferably greater than 11, and most preferably greater than 12. Particularly successful nonionic surfactants were ethoxylated fatty acid esters. Preferred ethoxylated fatty acid esters are selected from the group consisting of polyglycerin fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene castor oils, polyoxyethylene secondary alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl amines where the

BAD ORIGINAL

- alkyl groups range from 6 to 40 carbon atoms and may be independently selected, polyoxethylene alkyl amides where the alkyl groups range from 6 to 40 carbon atoms and the alkyl groups may be independently selected, amphoteric betaine surfactants, and polyoxethylene lanolins. A particularly preferred group of nonionic surfactants is the group consisting of, POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, and POE(20) sorbitan mono-palmitate. Another preferred group of surfactants which may be used to compatibilize the anionic emulsion with cationic surfactants is the group consisting of lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxymethylimidazolinium betaine, sodium N-lauroyl sarcosine, and lanolin derivatives of quaternary ammonium salts. Both of these groups of surfactants function to compatibilize the anionic emulsion with cationic surfactants.
- Having treated the anionically emulsion polymerized silicone emulsion with a nonionic surfactant having an HLB greater than 9, the emulsion is subsequently converted to a cationic emulsion by treatment with a cationic surfactant selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides or sulfates and alkyl trimethyl ammonium halides or sulfates, where the alkyl group ranges from eight to thirty carbon atoms. A particularly preferred group of cationic surfactants is selected from the group consisting of cetyltrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, benzalkonium chloride, and methylpolyoxyethylene(15)cocammonium chloride (ETHOQUAD C/25®).

It is to be noted that strongly basic anionic surfactants, such as carboxylates will not perform satisfactorily in the process of the present invention. The process of the present invention simultaneously depends on the beneficial interaction of the properties of the anionic surfactant, the compatibilizing surfactant and the cationic surfactant.

All of the United States patents referred to herein before or herein after are herewith specifically incorporated by reference.

BAD ORIGINAL

Experimental

Example 1: Anionic Polymerization with Dodecylbenzene Sulfonic Acid (DDBSA):

To a six liter stainless steel beaker was charged 1,500 g of octamethylcyclotetrasiloxane (D₄ or tetramer), 2,250 g water, and 15 g dodecylbenzene sulfonic acid. The mixture of tetramer, water, and acid was blended to insure uniformity using a high shear "Willems Polyton ®" mixer.

5 It is to be noted that other high shear mixers such as a Gaullin ® colloid mill are suitable. The mixture was then homogenized using a Gaullin Homogenizer ® at 7,500 psig. After full homogenization was achieved, the mixture was transferred to a five liter three neck round bottom flask equipped with a heating mantle, thermometer, condenser, thermal regulator, 10 and agitator. The mixture was maintained at a temperature of 86 °C for a period of three hours to allow polymerization to occur. Analysis of the reaction mixture after polymerization indicated a solids content of 35.4%. In order to increase the polymer molecular weight and thereby the polymer viscosity, the reaction mixture was cooled to a temperature of 22 to 23 °C and 15 held at that temperature for a period of thirteen hours. The reaction mixture, which is an emulsion, is cooled while the acid catalyst is still active in order to allow the polymer viscosity to stabilize at about one million centipoise. Mean particle size of this emulsion was less than 0.3 microns. The dodecylbenzene sulfonic acid was neutralized with base and 36 g of an aqueous 10 wt % solution of sodium carbonate, resulting in a final emulsion 20 pH of about 7.

Example 2: Various Polymer Viscosities:

Following the polymerization procedure outlined in example 1; utilizing the ratio of 100 parts of octamethylcyclotetrasiloxane, 1 part dodecylbenzene sulfonic acid, and 150 parts of water, followed by 25 neutralization with aqueous sodium carbonate solution; and a primary polymerization temperature of 85 °C maintained for a period of three hours, the secondary polymerization temperature was varied for a holding period of twenty-four hours to vary the molecular weight of the resultant polymer, resulting in a variation of polymer viscosities.

BAD ORIGINAL

Table I: Polymer Viscosities as a Function of Secondary Polymerization Temperature

<u>Secondary Polymerization Temperature</u>	<u>Polymer Viscosity</u>
0°C	cps at 25°C
5	3,760,000
15	2,264,000
25	934,000
35	323,000

The results in Table I indicate that secondary polymerization temperature has a marked effect on polymer viscosity and that as the secondary polymerization temperature is lowered polymer viscosity increases.

Example 3: Anionic Polymerization with Xylene Sulfonic Acid and Surfactant:

Utilizing the procedure of example, polymerization was attempted with 400 g of tetramer, 30 g of 40% xylene sulfonic acid as the sodium salt, 600 g water and 0.54 g sulfuric acid. This mixture would not form a homogeneous emulsion under conditions of high shear mixing, separating upon discontinuing the mixing. An additional 11 g of an anionic surfactant, sodium lauryl sulfate, was added which enabled the formation of a stable emulsion. The primary polymerization conditions were initially 86 °C for a period of four hours, resulting in a mean particle size of 0.23 microns and a solids content of 15.4%. Heating was continued for an additional seven hours. Since there was noticeable free oil on the surface of the reaction mixture after this period of time, the mixture was discarded since this is undesirable.

Example 4: Anionic Polymerization with Alkyl Sulfonic Acid and Surfactant:

Utilizing the process and equipment described in example 1, an emulsion was prepared from 30 g of 40% alkyl (C₁₄-C₁₆) olefin sulfonate as the sodium salt, 400 g tetramer, 600 g water and 0.75 g sulfuric acid. The mixture was vigorously blended, homogenized at 7,500 psig, and polymerized at 86 °C for seven hours and cooled to 22 to 23 °C for fourteen hours. The resulting polymer viscosity was approximately 1,000,000 cps and the emulsion contained 35.6 wt % solids with an average particle size of 0.2 micron. There was no free oil observed.

BAD ORIGINAL

Example 5: High Solids Anionic Emulsion Polymerization using Dodecylbenzene Sulfonic Acid:

Utilizing the process and equipment described in example 1, an emulsion was prepared using 1.2 parts by weight of dodecylbenzene sulfonic acid, 40 parts by weight water, and 54 parts by weight tetramer. Initial polymerization was conducted for a period of three hours at a temperature of 5 85 to 88 °C. The secondary polymerization step was conducted at a temperature ranging from 16 to 22 °C for a period of time ranging from about five to about seven hours. The emulsion was neutralized with 10 wt. % aqueous sodium hydroxide. The viscosity of the polymer prepared ranged from about 1 to 2,000,000 cps. The solids content of emulsions 10 resulting from this high solids content synthesis was about 54% with a mean particle size ranging from 0.23 to 0.28 microns, an emulsion viscosity below about 7,000 cps with a pH ranging from about 7 to about 9.

Emulsions prepared by this method have been found to be compatible with preservatives such as Germaben II ® (Sutton laboratories), Glycacil-L ® (Lonza), and Kathon II/ICP® (Rohm & Haas). Emulsion viscosity is controllable with Witco 1250® surfactant (Witco Chemical Co.).

Examples 6 and 7 represent the experiments where it was discovered that anionically polymerized emulsion polymers could be converted to cationic emulsions by the proper choice of surfactants.

Example 6: Anionic Polymerization with Dodecylbenzene Sulfonic Acid with Emulsion Stabilizers:

20 To an emulsion prepared as in example 1 using 100 parts by weight tetramer, 1 part by weight of dodecylbenzene sulfonic acid, 150 parts by weight water, neutralized with 2.4 parts by weight of 10 wt. % aqueous sodium carbonate resulting in a polymer viscosity of about 1,000,000 was added 2 parts by weight of methylpolyoxyethylene(15)cocammonium 25 chloride (Ethoquad C/25® from Armak and 2 parts by weight of POE(18)®, nonylphenylether. The emulsion was agitated for a period of one hour followed by the addition of 2 parts by weight of 30% aqueous cetyltrimethylammonium chloride. This emulsion was stabilized by using an nonionic-cationic surfactant mixture.

P&P ORIGINAL

Example 7: Anionic Polymerization with Dodecylbenzene Sulfonic Acid with Emulsion Stabilizers:

To a base emulsion prepared as in example 1, having a polymer viscosity of about 1,000,000 cps, was added 4 parts by weight POE 18 ®, nonylphenylether followed by agitation for a period of one hour followed by the addition of 2 parts by weight of cetyltrimethylammonium chloride (6.6 parts by weight of a 30% aqueous solution). This emulsion was stabilized by using an nonionic-cationic surfactant mixture.

Example 8: Evaluation of Amphoteric Cationic Surfactant Mixtures:

Other surfactant mixtures were evaluated in order that stable cationic emulsions might be prepared from emulsions prepared via an anionic polymerization. The surfactants that enable the conversion of a so-called anionic emulsion to a cationic emulsion are categorized as medium surfactants. Those surfactants evaluated were:

Amphoteric surfactant:

lauryldimethylaminoacetic acid betaine
coco fatty amide propyldimethylaminoacetic acid betaine
2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium
betaine

Anionic surfactant:

N-lauroyl sarcosine
sodium N-lauroyl sarcosine

Cationic surfactant:

lanolin derivatives of quaternary ammonium salts
methylbis(2-hydroxyethyl)oleylammonium chloride

Nonionic surfactant:

(POE = polyethylene oxide)
POE(4) lauryl ether
POE(9) lauryl ether
POE(23) lauryl ether
POE(6) stearyl ether
POE(20) stearyl ether
POE(6) sorbitan mono-oleate
POE(6) sorbitan mono-stearate
POE(20) sorbitan mono-palmitate

To a polymer emulsion prepared by anionic polymerization as described in example 1 and having an approximate polymer viscosity of about 1,000,000 cps was added 4 parts by weight of a so-called medium surfactant selected from the forgoing list. The emulsion was blended for a period of time of about one hour. If satisfactory dispersion was achieved, this was followed by the addition of 2 parts by weight of cetyltrimethylammonium chloride (6.6 parts by weight 30% aqueous solution).

The following results were obtained:

- 1) POE(6) stearyl ether and POE(6) sorbitan mono-stearate were difficult to dissolve in the anionic emulsion; consequently no attempt was made to add the cationic surfactant.
- 2) methylbis(2-hydroxyethyl)oleylammonium chloride broke the anionic emulsion and is therefore not suitable for the purposes attempted.
- 3) N-lauroyl sarcosine and POE(6) sorbitan mono-oleate were successfully added to the anionic emulsion, however when the cetyltrimethylammonium chloride, cationic surfactant, was added the resultant emulsion broke, and these two surfactants are therefore not suitable for the purposes attempted.
- 4) Lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, sodium N-lauroyl sarcosine, lanolin derivatives of quaternary ammonium salts, POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, and POE(20) sorbitan mono-palmitate

Example 9: Selection of Other cationic Surfactants with Medium Surfactants:

Other cationic surfactants were evaluated using the procedure of example 8, the emulsions prepared as in example 1, and the medium surfactants found to be compatible with cetyltrimethylammonium chloride. The following cationic surfactants were evaluated:

- cetyltrimethylammonium chloride
- cetyltrimethylammonium chloride
- stearyltrimethylammonium chloride
- di-stearyl-di-methylammonium chloride
- benzalkonium chloride
- stearyl-di-methylbenzylammonium chloride:

BAD ORIGINAL

with the following results:

1) di-stearyl-di-methylammonium chloride and stearyl-di-methylbenzylammonium chloride were difficult to dissolve in the blend and were therefore not considered acceptable.

5 2) cetyltrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, and benzalkonium chloride dispersed well, yielding acceptable cationic anionically emulsion polymerized emulsions with acceptable appearance and stability.

10 In summary, anionically emulsion polymerized silicone polymer emulsions may be converted to cationic emulsions by treatment with a medium surfactant selected from the group consisting of:

15 lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, sodium N-lauroyl sarcosine, lanolin derivatives of quaternary ammonium salts, POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, and POE(20) sorbitan mono-palmitate followed by treatment with a cationic surfactant selected from the group consisting of cetyltrimethylammonium chloride, cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, and benzalkonium chloride.

BAD ORIGINAL

Claims

1. A stable cationic silicone oil-in-water emulsion comprising:

(a) a silicone polymer having a viscosity ranging from about 10,000 to 10,000,000 centistokes;

5 (b) an anionic surfactant selected from the group consisting of alkyl, aryl and alkaryl sulfonic acids where the alkyl group ranges from 1 to about 20 carbon atoms, the aryl groups range from 6 to 30 carbon atoms, and the alkaryl groups range from 7 to about 50 carbon atoms;

(c) a compatibilizing surfactant having a hydrophilic lipophilic balance ratio of about 9 or greater; and

10 (d) a cationic surfactant selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides, mono-methyl ethoxylated ammonium sulfate, alkyl trimethyl ammonium halides, and alkyl trimethyl sulfate where the alkyl group of said cationic surfactant ranges from about 9 to about 30 carbon atoms.

2. The composition of claim 1 wherein the compatibilizing surfactant is selected from the group consisting of polyglycerin fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene castor oils, polyoxyethylene secondary alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl amines where the alkyl group is independently selected and ranges from 6 to 40 carbon atoms,

5 polyoxyethylene alkyl amides where the alkyl group is independently selected and ranges from 6 to 40 carbon atoms, polyoxyethylene lanolins, POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, POE(20) sorbitan mono-palmitate, amphoteric betaine surfactants, lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, sodium N-lauroyl sarcosine, and

10 lanolin derivatives of quaternary ammonium salts.

15 3. The composition of claim 1 or claim 2 where the anionic surfactant is selected from the group consisting of alkyl, aryl, and alkylaryl sulfonic acids, where the alkyl groups are 1 to 20 carbon atom alkyl groups and the aryl groups are 6 to 30 atom aryl groups.

BAD ORIGINAL

4. The composition of any preceding claim where the cationic surfactant is selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides, mono-methyl ethoxylated quaternary ammonium sulfate, alkyl trimethyl ammonium halides where the alkyl group ranges from eight to thirty carbon atoms and alkyl trimethyl ammonium sulfate where the alkyl group ranges from eight to thirty carbon atoms.
5. A process for making a stable cationic silicone oil-in-water emulsion comprising:
- 5 1) blending a mixture of silicones selected from the group consisting of cyclic silicone oligomers, mixed silicone hydrolyzates, silanol stopped oligomers, higher molecular weight silicone polymers, and functionalized silicones with
- 10 2) water, and
- 10 3) an anionic surfactant;
- 10 4) heating the blend to a temperature ranging from about 75 to about 98 °C for a period of time ranging from about 1 hours to about 5 hours;
- 15 5) cooling the heated blend to a temperature ranging from 0 to about 25 °C for a period of time ranging from about 3 hours to about 24 hours;
- 15 6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactants having a hydrophilic lipophilic balance (HLB) ratio greater than 9; and
- 15 7) adding a cationic surfactant.
- 6.. The process of claim 5 wherein the compatibilizing surfactant is selected from the group consisting of polyglycerin fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene castor oils, polyoxyethylene secondary alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl ethers where the alkyl group ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl amines where the alkyl group is independently selected and ranges from 6 to 40 carbon atoms, polyoxyethylene alkyl amides where the alkyl group is independently selected and ranges from 6 to 40 carbon atoms, polyoxyethylene lanolins, POE(4) lauryl ether, POE(9) lauryl ether, POE(23) lauryl ether, POE(20) stearyl ether, POE(20) sorbitan mono-palmitate, lauryldimethylaminoacetic acid betaine, coco fatty amide propyldimethylaminoacetic acid betaine, 2-alkyl-N-carboxymethyl-N-hydroxyethylimidazolinium betaine, sodium N-lauroyl sarcosine, and lanolin derivatives of quaternary ammonium salts.

BAD ORIGINAL

7. The process of claim 5 or claim 6 where the anionic surfactant is selected from the group consisting of alkyl, aryl, and alkylaryl sulfonic acids, where the alkyl groups are 1 to 20 carbon atom alkyl groups and the aryl groups are 6 to 30 atom aryl groups.
8. The process of any one of claims 5 to 7 where the cationic surfactant is selected from the group consisting of mono-methyl ethoxylated quaternary ammonium halides, mono-methyl ethoxylated quaternary ammonium sulfate, alkyl trimethyl ammonium halides where the alkyl group ranges from eight to thirty carbon atoms and alkyl trimethyl ammonium sulfate where the alkyl group ranges from eight to thirty carbon atoms.
9. A personal care product comprising the emulsion of any one of claims 1 to 4.
10. A process for the manufacture of personal care products comprising the process of any one of claims 5 to 8.



Application No: GB 9615231.9
Claims searched: 1-10

Examiner: Diane Davies
Date of search: 4 November 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3T: THC, THF

Int Cl (Ed.6): C08G 77/06, 77/08, 77/10: C08L 83/00

Other: Online: CAS-ONLINE, EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	EP 0463431 A (Dow Corning Corp.) Whole document: preparing silicone emulsions by using a nonionic surfactant of HLB of 10-19 and a second surfactant which may be nonionic, anionic or cationic.	
A	Abstracts of JP 07173294 A (Shinetsu Chemical Ind. Ltd.) Stable oil-in-water polysiloxane emulsion by using an ionic emulsifying agent and then adding a non-ionic emulsifying agent.	
X	Abstracts of JP 07041416 A (Shiseido Co. Ltd.) Stable emulsified composition containing siloxane, and possibly a non-ionic surfactant, cationic surfactant and anionic surfactant.	1-4
A	Abstracts of JP 05311575 A (Sanyo Chem. Ind. Ltd.) Aqueous emulsion of a dimethylsiloxane with a sulpho-succinic anionic surfactant, a cationic surfactant and a nonionic surfactant.	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.